

HIGH MECHANICAL AND OPTICAL PERFORMANCE ILLUMINATION  
SYSTEM

5 The present invention relates to the special shaping of  
phosphore particles known elsewhere, capable of  
guaranteeing, on the one hand, high mechanical and  
optical properties, such as mechanical strength under  
the most exacting handling conditions, strength impact  
10 resistance, abrasion resistance, crush and crack  
resistance and, possibly, delamination in the case of a  
deposit on a substrate, shear strength, flexural  
strength, etc. and, on the other hand, transparency,  
the virtual absence of haze, controlled light  
transmission between values that can approach 100% and  
15 low values in the case of highly scattering materials,  
optical homogeneity, absence of degradation and  
yellowing, particularly under the effect of excitation,  
etc.

20 The term phosphore particles refers to particles that  
are able to emit light, particularly in the long  
wavelength region of the visible spectrum, under the  
effect of excitation by UV radiation, an electron beam,  
X-rays, gamma radiation or an electric field, these  
25 particles having a size, for example, that lies between  
a few nanometers and a few microns, and being used  
particularly in lamps in the form of powdered masses.

In addition, application FR-A1-2 829 481 mentions  
30 separately the coating of phosphore particles with a  
stabilizing sodium silicate film on the one hand and,  
on the other hand, the deposition of dispersions  
possibly with other phosphores, in the form of  
transparent films on a glass substrate. However, the  
35 document does not specify how a film, or all the more a  
transparent film, is to be obtained.

The invention now provides composites of phosphore  
particles capable of preserving integrity of state and

shape over long periods, under normal conditions of use (assembly, installation, cleaning, etc.).

This objective is achieved by the invention, the  
5 subject of which is an illumination system consisting of phosphore particles dispersed in a solid, durable matrix, while enabling it to be handled by a user.

Phosphore particles falling within the scope of the  
10 invention are, for example:

$\text{Ca}_{10}(\text{PO}_4)_6\text{FCl:Sb,Mn}$   
 $(\text{Sr,Mg})_2\text{P}_2\text{O}_7:\text{Eu}$   
 $\text{Sr}_2\text{P}_2\text{O}_7:\text{Eu}$   
 $\text{Sr}_5(\text{PO}_4)_3\text{Cl:Eu}$   
15  $(\text{Sr,Ca,Ba})_5(\text{PO}_4)_3\text{Cl:Eu}$   
 $\text{BaMg}_2\text{Al}_{16}\text{O}_{27}:\text{Eu}$   
 $\text{BaMg}_2\text{Al}_{16}\text{O}_{27}:\text{Eu,Mn}$   
 $\text{CaWO}_4$   
 $\text{CaWO}_4:\text{Pb}$   
20  $\text{Ba}_2\text{P}_2\text{O}_7:\text{Ti}$   
 $(\text{Ba,Ca})_5(\text{PO}_4)_3\text{Cl:Eu}$   
 $\text{Zn}_2\text{SiO}_4:\text{Mn}$   
 $\text{Y}_3\text{Al}_5\text{O}_{12}:\text{Ce}$   
 $\text{MgAl}_{11}\text{O}_{19}:\text{Ce,Tb,Mn}$   
25  $\text{LaPO}_4:\text{Ce,Tb}$   
 $\text{Y(P,V)O}_4:\text{Eu}$   
 $3.5\text{MgO}.0.5\text{MgF}_2.\text{GeO}_2:\text{Mn}$   
 $(\text{Sr,Mg})_3(\text{PO}_4)_2:\text{Sn}$   
 $\text{Y}_2\text{O}_3:\text{Eu}$   
30  $\text{CaSiO}_3:\text{Pb,Mn}$   
 $\text{BaSi}_2\text{O}_5:\text{Pb}$   
 $(\text{Ba,Sr,Mg})_3\text{Si}_2\text{O}_7:\text{Pb}$   
 $\text{SrB}_4\text{O}_7:\text{Eu}$   
 $\text{YPO}_4:\text{Ce}$   
35  $\text{LaPO}_4:\text{Ce}$   
 $(\text{Mg,Ba})\text{Al}_{11}\text{O}_{19}:\text{Ce}$   
 $\text{LiAlO}_2:\text{Fe}$   
 $\text{ZnS:Ag,Cl}$   
 $\text{ZnS:Mn}$

	ZnS:Ag, Al
	ZnS:Cu, Al
	ZnS:Cu, Au, Al
	Y <sub>2</sub> O <sub>2</sub> S:Eu
5	ZnS:Ag+ (Zn, Cd) S:Cu
	ZnS: (Zn)
	(KF, MgF <sub>2</sub> ) :Mn
	(Zn, Cd) S:Ag
	(Zn, Cd) S:Cu
10	ZnO:Zn
	(Zn, Cd) S:Cu, Cl
	ZnS:Cu
	ZnS:Cu, Ag
	MgF <sub>2</sub> :Mn
15	(Zn, Mg) F <sub>2</sub> :Mn
	Zn <sub>2</sub> SiO <sub>4</sub> :Mn, As
	Gd <sub>2</sub> O <sub>2</sub> S:Tb
	Y <sub>2</sub> O <sub>2</sub> S:Tb
	Y <sub>3</sub> (Al, Ga) <sub>5</sub> O <sub>12</sub> :Ce
20	Y <sub>2</sub> SiO <sub>5</sub> :Ce
	Y <sub>3</sub> Al <sub>5</sub> O <sub>12</sub> :Tb
	Y <sub>3</sub> (Al, Ga) <sub>5</sub> O <sub>12</sub> :Tb
	InBO <sub>3</sub> :Tb
	InBO <sub>3</sub> :Eu
25	ZnS:Ag
	Y <sub>2</sub> SiO <sub>5</sub> :Tb
	(Zn, Cd) S:Cu, Cl+ (Zn, Cd) S:Ag, Cl
	InBO <sub>3</sub> :Tb+InBO <sub>3</sub> :Eu
	ZnS:Ag+ZnS:Cu (or ZnS:Cu, Au) +Y <sub>2</sub> O <sub>2</sub> S:Eu
30	InBO <sub>3</sub> :Tb+InBO <sub>3</sub> :Eu+ZnS:Ag
	Gd <sub>2</sub> O <sub>2</sub> S:Eu
	(Y, Sr) TaO <sub>4</sub>
	(Y, Sr) TaO <sub>4</sub> :Gd
	(Y, Sr) TaO <sub>4</sub> :Nb
35	BaFCl:Eu
	BaFBr:Eu
	BaMgAl <sub>10</sub> O <sub>17</sub> :Eu
	YBO <sub>3</sub> :Tb
	BaAl <sub>12</sub> O <sub>19</sub> :Mn

(Y,Gd)BO<sub>3</sub>:Eu  
YBO<sub>3</sub>:Eu  
Sr<sub>4</sub>Al<sub>14</sub>O<sub>25</sub>:Eu,Dy  
SrAl<sub>2</sub>O<sub>4</sub>:Eu,Dy  
5 CaAl<sub>2</sub>O<sub>4</sub>:EU,Nd  
Y<sub>2</sub>O<sub>2</sub>S:Eu,Mg,Ti

These phosphore particles or these mixtures of  
phosphore particles are characterized by the emission  
10 of long wavelength radiation in the visible region,  
corresponding to different colors, white light, or in  
the IR or UV. The last three mentioned in the above  
list are notable for the intensity, persistence and  
duration of their activity, after any excitation source  
15 has been removed, in particular at night.

The invention therefore makes it possible to provide  
handlable, reliable, strong solid illuminating objects  
that can coat a multitude of forms, such as a coating  
20 on a substrate, capable of illuminating in various  
colors, opening the way to the most novel and varied  
esthetic or artistic creations.

Preferably, the particles are phosphores within the  
25 visible region, in which most of the applications  
envisaged below present the greatest interest.

The particles can be excited by electromagnetic  
radiation in the UV, visible, IR region or by X-rays or  
30 by gamma rays, or by a beam of particles (electrons,  
ions) or by an electric field. Excitation by UV may be  
derived from the deexcitation of a plasma or of an  
ionized gas.

35 According to a preferred embodiment, the matrix is  
inorganic and comprises, in a particularly preferred  
manner, lithium silicate. It should be stated that  
sodium silicates, and to a lesser extent potassium  
silicates, are suitable if need be for an opaque

illumination system, lithium silicate being particularly recommended for a transparent illumination system. Accordingly, it has been observed with sodium silicate that there is a migration to the surface of a  
5 very hygroscopic and scattering crust based on sodium hydroxide that is continually regenerated. Lithium silicate proves to be notable for the possibility of distributing therein, in a uniform manner, high concentrations of phosphore particles in the most  
10 separated state possible, as well as for its compatibility with many substrates, including glass. On account of the fact that the matrix comprises lithium silicate, it will be understood that, in reality, the matrix is a product of the partial or total conversion  
15 of lithium silicate, in particular into silica, in which lithium silicate and/or lithium remain entirely detectable.

According to another embodiment, the matrix comprises a  
20 product of the polymerization/polycondensation of a silicon alkoxide such as tetraethoxysilane (TEOS), tetramethoxysilane (TMOS), methyltriethoxysilane (MTEOS) and the like. These precursors of the matrix provide excellent conditions for compatibility with  
25 many phosphore particles, among those previously mentioned.

In a practical and effective embodiment of the invention, the matrix is in the form of a thin layer  
30 adhering to a substrate consisting in particular of glass, for example in the form of a sheet, but also of a slab intended to constitute an electronic display screen, a tube, in particular for lighting, fiber or fabric or plastic. For the latter, reference may be  
35 made to any generally transparent plastic such as polycarbonate, polyvinyl butyral, a polyolefin such as polyethylene or polypropylene, poly(ethylene terephthalate), polyurethane, acrylic polymer such as poly(methyl methacrylate), an ionomer resin, various

copolymers, etc., the use of which is of course limited by possible formation of a thin layer at a temperature capable of affecting or degrading the plastic.

5 The invention comprises two main variants.

According to the first variant, the phosphore particles are in aqueous suspension and their size is at most equal to 100 nm, preferably 30 nm, preferably 10 nm,  
10 and the assembly that they form with the matrix is transparent.

According to the second variant, the size of the phosphore particles lies between 0.5 and 10  $\mu\text{m}$ , it  
15 being possible for particles scattering visible light to be then advantageously incorporated in the matrix (particles may be involved other than phosphore particles having a size of, in particular, between 100 nm and 1  $\mu\text{m}$ , in particular between 300 and 700 nm,  
20 such as alumina, or phosphore particles themselves; these light-scattering particles are dielectric, semiconduction or conducting particles).

Thus, phosphore particles with a size between 30 and  
25 500 nm are not excluded from the invention, those having in particular a size at least equal to 400 nm that are capable of scattering visible light making it unnecessary to add other scattering particles.

30 In a particularly advantageous embodiment of the illumination system of the invention, in the case where the matrix is in the form of a thin layer adhering to a substrate, the latter is capable of exciting phosphore particles, and is in particular an electroconductor, in  
35 particular of the UV electroluminescent type.

In an equally advantageous embodiment, the substrate is capable of emitting radiation with a wavelength in the visible region under suitable excitation. It is then,

for example, made of glass with a cerium content, capable of emitting blue light under ultraviolet radiation.

5 According to another alternative of the design of the illumination system, two cases may be distinguished in which:

- 10 - the phosphore particles emitting different wavelengths are associated, separated from each other and homogenized, so as to produce white light, yellow light, etc., on the one hand; and
- the phosphore particles that are identical or emit different wavelengths are combined in variable compositions and/or concentrations, so as to form  
15 signs such as written or similar signs, or for any other, especially decorative, purpose.

The main processes for preparing the illumination system of the invention consist of:

- 20 - cold deposition processes by means of a liquid, such as spray coating, flow coating, dip coating, spin coating, screen printing, followed by a heat treatment at 100-650°C, for example (annealing, tempering, etc.) according to the nature of the  
25 matrix; or
- a vacuum deposition process.

In addition, other subjects of the invention are:

- 30 - the application of an illumination system as described above to a transparent device;
- the application of the illumination system to a light-scattering device;
- the application of the illumination system to a lamp, in particular a thin one, or to a device  
35 illuminating at night, in particular for signs, or for decorative purposes or to a flat lamp as described in the application WO 04/15739;
- the application of the illumination system to monolithic, laminated, single glazing or multiple

glazing designed for buildings, to a transport vehicle, such as an automobile rear window, side window or roof, to any other terrestrial or aquatic vehicle or aircraft, to street furniture, such as a bus shelter, to a road sign or to an advertisement panel, to an aquarium, to a store window, to a glasshouse, to interior furniture, to a mirror, to a screen for a display system of the computer type, to a television, to a telephone, to electrically controllable glazing such as electrochromic glass, to liquid crystals, to electroluminescent material or to photovoltaic glass.

It is stated that in this last application, the association of the illumination system with glazing is compatible with all known practical applications thereof, either on the same face as that supporting the illumination system, above or below, or on other faces of the glazing, namely a hydrophobic/oleophobic, hydrophilic/oleophilic, anti-soiling photocatalytic layer, a multilayer reflecting thermal radiation (solar protection layer) or IR (low-e layer), antireflection layer, etc.

As a valuable example, mention may be made of glazing that separating, for example, an enclosure in a building from the outside atmosphere, the inner face of which is illuminating according to the invention, and the outer face of which is electrochromic, that is to say capable of being darkened by applying a voltage to the layer. In this way, the functionality obtained is that of illuminating the interior while blocking off external light.

In the illuminating glazing application according to the invention, the glazing guarantees maximum transparency and maximum optical quality in the absence



of excitation, and constitutes an illuminating surface in the presence of excitation.

5 The screen application for a display system can be generalized to any application requiring a light source and means of treatment thereof, in the form of a light box.

10 It consists in particular of backlight.

The invention is illustrated by the following examples of embodiments.

**EXAMPLE 1**

15 YVO<sub>4</sub>:Eu nanoparticles were first of all synthesized by a colloidal method.

20 The entire synthesis of colloidal solutions was carried out in water at a temperature of 60°C. The insoluble citrate complex was formed by mixing 0.75 equivalents of sodium citrate (0.1 mol/l, 15 ml) with 1 equivalent of (Y,Eu)(NO<sub>3</sub>)<sub>3</sub> (0.1 mol/l, 20 ml). Addition of 0.75 equivalents of an Na<sub>3</sub>VO<sub>4</sub> solution with a pH of 12.5  
25 (0.1 mol/l, 15 ml) caused the precipitate to dissolve and the reaction to start. The pH of the clear solution obtained was 7.6. At the end of 30 minutes of reaction, heating was stopped. The colloidal solution obtained was then dialyzed in water at neutral pH so as to  
30 eliminate various counterions (Na<sup>+</sup>, NO<sub>3</sub><sup>-</sup>) or any unreacted species. Following the dialysis step, the concentration of the colloidal solution was of the order 10<sup>-2</sup> mol/l.

35 The colloidal solutions were then concentrated by evaporation to dryness under mild conditions (40°C under vacuum). The powder obtained was easily redispersed in a very small quantity of water which enabled very concentrated colloidal solutions to be

obtained (up to 2 mol/l, that is 400 g/l) Moreover, the size measured by light scattering after redispersion ( $10\pm 3$  nm) was identical to that of the colloid obtained after dialysis: the colloids underwent no aggregation during the concentration step. As a consequence, the concentrated colloidal solutions were optically transparent.

Transparent luminescent films were prepared in the following way: 0.2 to 1 ml of lithium silicate (30% by mass in water, pH 12) was added to 4 ml of the concentrated colloidal solution of  $\text{YVO}_4\text{:Eu}$  nanoparticles. The sol obtained was filtered (glass fiber prefilter and  $0.45\text{ }\mu\text{m}$  filter) and then deposited by centrifuging (speed of rotation 1000 rpm for 60 seconds) onto a float glass substrate ( $5 \times 5\text{ cm}^2$ ). The thin films obtained were finally annealed at  $450^\circ\text{C}$  for 12 hours. The purpose of this heat treatment was to consolidate the film mechanically and to increase the luminescence (elimination of hydroxyl groups that inhibit the luminescence of europium ions). After annealing, the thin films were perfectly transparent and had a thickness of between  $0.2$  and  $0.7\text{ }\mu\text{m}$ .

The thin films were placed under a UV lamp emitting at 254 nm. Red luminescence, characteristic of europium ions, was observed within the  $\text{YVO}_4$  matrix. Luminance measurements were carried out and confirmed what was visually observed: light emission was more intense on the cut edge of the film than in the center. Indeed, the luminance was  $5\text{ Cd/m}^2$  at the center whereas it was  $20\text{ Cd/m}^2$  at the cut edge.

## **EXAMPLE 2**

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This example describes the preparation of scattering luminescent layers.

12.8 g of alumina particles with a mean diameter of 500 nm were added to 176 g of deionized water together with 0.24 g of polyacrylic acid (50% by weight solution in water). Sodium hydroxide was then added until a pH  
5 of 10 was reached. 5 g of  $\text{LaPO}_4\text{:Ce,Tb}$  particles with a mean diameter of 2  $\mu\text{m}$ , sold by Nichia, were then added. The mixture was then homogenized in a turbine for 5 minutes. 11 g of lithium silicate (30% by weight solution in water) were then added. After 5 minutes of  
10 homogenization in a turbine, the mixture was deposited on a  $10 \times 10 \text{ cm}^2$  glass substrate by flow coating.

Drying was carried out under an IR lamp (temperature of the coating approximately  $80^\circ\text{C}$ ). The coating obtained  
15 had a  $T_L$  of 60% and haze close to 100%.

Green luminescence produced in the coating was observed under photoexcitation at 257 nm.